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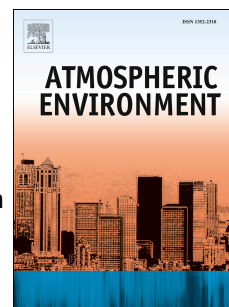
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Isotopic signatures in atmospheric particulate matter suggest important contributions from recycled gasoline for lead and non-exhaust traffic sources for copper and zinc in aerosols in London, United Kingdom

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**Abstract**

The aim of this study was to improve our understanding of what controls the isotope composition of Cu, Zn and Pb in particulate matter (PM) in the urban environment and to develop these isotope systems as possible source tracers. To this end, isotope ratios (Cu, Zn and Pb) and trace element concentrations (Fe, Al, Cu, Zn, Sb, Ba, Pb, Cr, Ni and V) were determined in PM<sub>10</sub> collected at two road sites with contrasting traffic densities in central London, UK, during two weeks in summer 2010, and in potential sources, including non-combustion traffic emissions (tires and brakes), road furniture (road paint, manhole cover and road tarmac surface) and road dust. The isotope signatures of other important sources (gasoline and exhaust emissions) were taken from previous published data. Iron, Ba and Sb were used as proxies for emissions derived from brake pads, and Ni, and V for emissions derived from fossil fuel oil.

The isotopic composition of Pb (expressed using  $^{206}\text{Pb}/^{207}\text{Pb}$ ) ranged between 1.1137 and 1.1364. The isotope ratios of Cu and Zn expressed as  $\delta^{65}\text{Cu}_{\text{NIST976}}$  and  $\delta^{66}\text{Zn}_{\text{Lyon}}$  ranged between -0.01 ‰ and +0.51 ‰ and between -0.21 ‰ and +0.33 ‰, respectively. We did not find significant differences in the isotope signatures in PM<sub>10</sub> over the two weeks sampling period and between the two sites, suggesting similar sources for each metal at both sites despite their different traffic densities. The stable isotope composition of Pb suggests significant contribution from road dust resuspension and from recycled leaded gasoline. The Cu and Zn isotope signatures of tires, brakes and road dust overlap with those of PM<sub>10</sub>. The correlation between the enrichments of Sb, Cu, Ba and Fe in PM<sub>10</sub> support the previously established hypothesis that Cu isotope ratios are controlled by non-exhaust traffic emission sources in urban environments (Ochoa Gonzalez et al., 2016). Analysis of the Zn isotope signatures in PM<sub>10</sub> and possible sources at the two sites suggests significant contribution from tire wear. However, temporary additional sources, likely high temperature industrial emissions, need to be invoked to explain the isotopically light Zn found in 3 out of 18 samples of PM<sub>10</sub>.

## 1. Introduction

Metals in atmospheric particulate matter (PM) are a serious concern as they induce adverse health effects. Cardiopulmonary diseases have been attributed to the capacity of inhaled particles and metals to cause inflammation and injury at the air-lung interface (Costa and Dreher, 1997; Chen and Lippmann, 2009; Gamble and Lewis, 1996; Jarup, 2003; Ozkaynak et al., 1996). Lead exposure damages the human central nervous system and kidneys, affects biochemical processes and impairs psychological and neurobehavioral functions (Tong et al., 2000). Zinc is associated with oxidative stress and a contributing factor in many chronic diseases (Prasad et al., 2004; Walsh et al., 1994), and Cu causes damage to proteins and lipids (Brewer, 2010). Thus, developing a full understanding of the major sources of metals in urban PM is critical to control toxic emissions in urban environments.

Previous studies analyzed the sources of multiple elements in urban PM by using conventional chemical techniques and receptor modeling methods such as principal component analysis (PCA) and positive matrix factorization (PMF). These suggested that industrial emissions, exhaust and non-exhaust traffic emissions and resuspended road dust are the major sources that contribute to the metal aerosol burden in large cities around the world including Birmingham, Thessaloniki, and Boston (Cooper and Watson, 1980; Harrison et al., 1997; Laden et al., 2000; Lin et al., 2010; Manoli et al., 2002; Polissar et al., 2001; Querol et al., 2001; Thurston and Spengler, 1985). Iron and Cr are often associated with the bulk matrix from road dust, Zn from tire and brake wear, and road dust re-suspension, Pb from the past use of leaded gasoline, Fe from brake drum abrasion, wear-off of engines, tires and brakes, and V and Ni with emissions from oil combustion (Garg et al., 2000; Hjortenkranz et al., 2007; Manoli et al., 2002; Thorpe et al. 2007; Thurston et al., 2011). Copper, Sb and Ba are abundant in brake lining materials whereas brakes, yellow road paint and road pavement are typically sources of Cr (Adachi and Tainosho, 2004; Garg et al., 2000; Hjortenkranz et al., 2007; Iijima et al., 2007; Rodriguez et al., 2004; Salma and Maenhaut, 2006; Thorpe and Harrison, 2008).

The success of using metal concentrations in combination with PCA and PMF to identify single sources of trace metals remains limited. PCA does not provide a unique solution because of its simplified approach and the results of PMF vary depending on different uncertainty structures (Samek et al., 2016). Consequently, the use of isotope ratios is widely investigated to improve source tracing in atmospheric particles (Wiederhold, 2015; Weiss et al., 2008). This approach was indeed highly successful for Pb, where isotopes identified leaded gasoline as the main source in urban PM in London, and despite the restrictions in the use of leaded gasoline in the 1980s, a contribution of 60% was still found in west London between 1995 and 1996 (Monna et al., 1997; Noble et al., 2008). Stable isotope systems have been tested for source apportionment of trace elements in PM such as Fe, Sr, Zn and Nd (Flament et al., 2008; Geagea et al., 2008; Majestic et al., 2009; Widory et al., 2010). Zinc isotopes in urban PM were studied in Metz (Cloquet et al., 2006), São Paulo (Gioia et al., 2008), and Barcelona and London (Ochoa Gonzalez et al., 2016). In Metz, the  $\delta^{66}\text{Zn}_{\text{Lyon}}$  in ambient PM collected in a bus and an urban waste incinerator showed similar values close to +0.12 ‰. In São Paulo, in contrast, Gioia et al. (2008) found lighter ratios and significantly larger variations in  $\delta^{66}\text{Zn}_{\text{Lyon}}$ , ranging between -1.05 and -0.46 ‰ in  $\text{PM}_{2.5-10}$  and between -1.13 and -0.07 ‰ in  $\text{PM}_{2.5}$ . In line with these findings, Ochoa Gonzalez et al. (2016) found isotopically light Zn in  $\text{PM}_{10}$  collected in Barcelona, with  $\delta^{66}\text{Zn}_{\text{Lyon}}$  ranging between -0.45 and -0.83 ‰, and isotopically heavy Cu in coarse PM collected in London during late autumn

and the winter season ( $\delta^{65}\text{Cu}_{\text{NIST976}}$  between +0.66 and +0.97 ‰) (Ochoa Gonzalez et al., 2016). The observed isotope signatures in the PM were associated with sources derived from combustion and smelting processes. Other studies are in line with this interpretation as they showed that residues and flue gas particles from metal refining and coal combustion are highly fractionated relative to the starting materials, with isotopically lighter Zn emitted in the PM (between -0.73 and -0.63 ‰) and heavy Zn remaining in the residues (up to +1.49 ‰) (Mattielli et al., 2009; Ochoa Gonzalez and Weiss, 2015; Sivry et al., 2008). These signatures seem to partially overlap with the isotope ratios of Zn in anthropogenic materials produced during low temperature processes like galvanisation which show  $\delta^{66}\text{Zn}_{\text{Lyon}}$  between +0.12 and +1.15 ‰ (Araújo et al., 2017; John et al., 2007). In summary, these studies suggested strongly that Cu and Zn isotopes can play an important role in the identification of emission sources from metal refining and combustion due to their larger fractionation, as well as Pb isotopes to assess the contribution from the past use of leaded gasoline.

The aim of this study was to improve our present knowledge on what controls the isotopic variability of Cu, Zn and Pb in urban PM and to critically assess the potential of these isotope systems for source tracing. To this end, we determined short-term temporal and spatial isotope variability of Cu, Zn and Pb in  $\text{PM}_{10}$  collected in 2010 in central London and in potential sources including road furniture (manhole cover, road paint and road tarmac surface), non-combustion vehicle sources (tire and brake wear) and road dust (that represents other potential sources deposited in the road environment). We collected possible sources and  $\text{PM}_{10}$  samples at a high and a low traffic density site over a 20-day sampling period during summer. The concentrations of trace elements including Fe, Sb, Ba, Cr, Ni, and V, and enrichment factors (EF) were combined with the isotope ratios of Zn, Cu and Pb to constrain possible contributions from sources. Finally, we critically compare the isotope data in  $\text{PM}_{10}$  and potential sources in London with previously published isotope signatures of other potential sources and PM from major urban cities.

## 2. Materials and methods

### 2.1. Sample collection

Samples of  $\text{PM}_{10}$  were collected for 48 h using a Partisol-Plus Model 2025 Sequential Air Sampler (Thermo Scientific, MA, USA) at two different road sites in central London between 8<sup>th</sup> July 2010 and 28<sup>th</sup> July 2010 at a height of 3.5 m. Nine samples (MR1-MR9) were collected at the heavily traffic street canyon Marylebone Road (denoted as MR) in London, with more than 80,000 vehicles per day and frequently congested (Charron and Harrison, 2005). Nine samples (NK1-NK9) were collected at a sampling location in North Kensington (denoted as NK) which is a lightly trafficked open urban site situated next to a school playground (Bigi and Harrison, 2010). The sampling site NK has an average daily traffic flow of 8,000 vehicles and the nearest road is more than 30 m away (Abdalmogith and Harrison, 2006). Polytetrafluoroethylene (PTFE) filters were used for  $\text{PM}_{10}$  collection and leached prior use for 2 days in 1.5 M sub-boiling distilled  $\text{HNO}_3$  at 100°C on a hotplate.

Potential sources for various metals were constrained following a critical literature review and included brake pads for Cu, Sb and Ba; tire wear and road dust for Zn, Fe, Pb and Cr; road paint and road surface for Cr (Adachi and Tainosho, 2004; Hjortenkrans et al., 2007; Thorpe and Harrison, 2008; Thorpe et al., 2007), and manhole covers for Zn (Fry et al., 2005). The isotopic composition of Zn and Pb from gasoline and vehicle exhaust emissions have been taken from the literature (Cloquet et al., 2006; Gioia et al., 2008; Monna et al.,

1997).

Three samples of road dust were taken at each site, one next to the PM sampling tube and two in the opposite directions from each sampling site. Approximately 30 g of road dust were taken using a brush and a pan previously cleaned; samples were sieved at 2 mm and then milled using an agate pestle and mortar for subsequent analysis. The road dust samples were taken during clear days without rainfall 24 h prior sample collection. Road furniture (manhole cover and road paint, two samples at each site; road tarmac surface, two samples at the NK site) were sampled within approximately 10 m of each aerosol sampling site and were stored in plastic bags. There were no natural soils exposed close to the sampling sites. There were manhole covers in the middle of the roads where the PM<sub>10</sub> were collected, as well on the side. There were approximately five manhole covers within 50 m.

Non-combustion vehicle sources, i.e., tear-off from tires and brakes, were characterized using a collection of used tires and new brake pads. Twelve individual car tires of common commercial brands were shredded and mixed in three sets (labelled as R43/54-1, R43/54-2 and R56/57-1) before analysis. The brake samples were scratched from the surface of two different brands of metallic brake pads commonly used. These include metallic pads HBP Ferodo for Peugeot and Renault cars, and FSB Halfords for Volkswagen family cars (labelled as HBP and FSB, respectively).

## 2.2. Sample preparation

The filters were weighed before and after the collection to determine the mass of material. The metals were leached from the filter with 5 ml of aqua regia for 24 hours followed by 10 ml of 0.5 M HNO<sub>3</sub> for 48 hours on a hotplate at 80°C. An ultrasonic bath was used for 1 hour every 12 hours to improve the removal efficiency. The filters were then washed with 5 ml 0.5 M HNO<sub>3</sub> three times. The two solutions were mixed and evaporated to dryness before further treatment. The standard reference material BCR-723 (road dust) and all the samples were digested using a conc. HNO<sub>3</sub>:HClO<sub>4</sub> mixture (1:4) in sealed PFA vials (Savillex, MN, USA) at 150°C in a hotplate for 24 hours. HClO<sub>4</sub> was used to favor the oxidation of the organic matter. The samples were dried and digested using a mixture of conc. HNO<sub>3</sub> and HF (1:4) on a hotplate at 140°C for another 24 hours. The solutions were taken to dryness again. The samples were re-fluxed in 300 µl of conc. HNO<sub>3</sub> and evaporated twice to remove the excess of fluorides. After re-dissolution in 2.5 ml of 0.5 M HNO<sub>3</sub>, 0.5 ml was used for concentration measurement using quadrupole ICP-MS and the remaining volume of each solution was prepared for anion exchange column separation of Pb, Cu and Zn.

All the experimental work was carried out in a Class 1000 clean lab and under Class 10 laminar flow hoods in the MAGIC laboratories at Imperial College London. Sub-distilled mineral acids (HNO<sub>3</sub> 15 mol l<sup>-1</sup>, HCl 6 mol l<sup>-1</sup>), commercial HF (40 % v/v Suprapur, Merck, Germany) and HClO<sub>4</sub> (70 % v/v Suprapur, Merck, Germany), and 18.2 MΩ·cm grade Millipore water (Bedford, MA, USA) were used throughout this study.

## 2.3. Concentration analysis and enrichment factors

The concentration of Fe, Al, Cu, Zn, Sb, Ba, Pb, Cr, Ni and V were determined using quadrupole ICP-MS (Varian, CA, USA). Table S1 shows the concentrations of Cu, Zn, Sb, Ba and Pb determined for BCR-723 (road dust) and the indicative values provided by the European Commission Joint Research Centre Institute for Reference Materials and Measurements. The analytical uncertainty of the concentration determinations for all



elements was better than 6% (n=5, 2SD) and the recoveries, relative to the indicative values were higher than 89 % with respect to the reference values for all the elements.

The EFs of the PM<sub>10</sub> were calculated to assist the source assessment study using Al as a proxy for the upper continental crust according to Eq. 1,

$$EF_C = \frac{C_{\text{sample}}/Al_{\text{sample}}}{C_{\text{crust}}/Al_{\text{crust}}} \quad [\text{Eq. 1}]$$

where C is the element of interest and C<sub>sample</sub>, Al<sub>sample</sub>, C<sub>crust</sub> and Al<sub>crust</sub> are the concentrations of C and Al in the sample and the continental crust. The average chemical composition of the upper continental crust was used as previously reported (Wedepohl, 1995).

#### 2.4. Isotope ratio analysis of Cu, Zn and Pb

Copper, Zn and Pb in all of the samples were separated from other matrix elements using ion exchange chromatography. The details of the Cu, Zn and Pb separation methods and sample treatment are described in detail elsewhere (Dong et al., 2013; Weiss et al., 2004) and summarized in the supplementary material. The isotope ratios were determined using a Nu Plasma multi collector ICP-MS (Nu Instruments Limited, UK) equipped with a Nu DSN-100 Desolvation Nebuliser System. The instrumental mass bias was corrected using standard-sample bracketing for Cu isotope ratio measurement (Peel et al. 2008), Tl doping for Pb isotope ratio measurements (Weiss et al., 2004) and a <sup>64</sup>Zn-<sup>67</sup>Zn double spike for Zn isotope ratio measurements (Arnold et al., 2010; Ochoa Gonzalez et al., 2016).

The total procedural blank was <4 ng for Cu and Zn, and < 80 pg for Pb. These contributions were less than 0.01% of the total element content in all samples analyzed and had no significant effect on the accuracy of the isotope ratio measurements. The Romil Cu and Romil Zn solutions were processed and measured with the samples and showed values of δ<sup>65</sup>Cu<sub>NIST976</sub> = +0.17 ± 0.10 ‰ (2SD, n=24) and δ<sup>66</sup>Zn<sub>Lyon</sub> = -9.12 ± 0.08 ‰ (2SD, n=20), respectively. These are within error relative to previous published values for Romil Cu (δ<sup>65</sup>Cu<sub>NIST976</sub> = +0.18 ± 0.06 ‰, n=19, Moeller et al., 2012; δ<sup>65</sup>Cu<sub>NIST976</sub> = +0.18 ± 0.05 ‰, n=4, Ochoa Gonzalez et al., 2016) and Romil Zn (δ<sup>66</sup>Zn<sub>Lyon</sub> = -9.14 ± 0.08 ‰, n=21, Chapman et al., 2006). During this study <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb for NIST-SRM 981 Pb (when treated as non-spiked standard) were 16.9372 ± 0.0021, 15.4954 ± 0.0021 and 36.7158 ± 0.0057 (n=50), respectively, which are in good agreement with previous published data (Weiss et al., 2004).

### 3. Results and discussion

#### 3.1. Source assessment based on concentrations and enrichment factors

The concentrations of PM<sub>10</sub> and of Fe, Cu, Al, Zn, Sb, Ba, Fe, Cr, Pb, Ni and V in PM<sub>10</sub> and local sources are shown in Table 1 and Table 2. The concentrations of PM<sub>10</sub> are approximately twice as high at the MR site (31±7 µg m<sup>-3</sup>) compared to the NK site (14±3 µg m<sup>-3</sup>). According to London Air, average hourly concentrations of PM<sub>10</sub> at the MR and NK sites over the sampling period during July 2010 are 40±15 µg m<sup>-3</sup> and 16±7 µg m<sup>-3</sup>, respectively (London Air Website, www.londonair.org.uk).

The concentrations and EFs of Fe, Cu, Zn, Sb, Ba and Cr in the PM<sub>10</sub> collected at the MR site are much higher than those at the NK site (Tables 1 and 3). These elements are highly enriched relative to natural dust



represented geochemically by the upper continental crust (Table 3), suggesting that they are derived from traffic related emissions. Iron, Cu, Zn, Sb and Ba are typically high in tires and brakes (McKenzie et al., 2009). The correlations between the  $EF_{Sb}$  and those of Fe, Cu, Zn and Ba (Figure 1) in  $PM_{10}$  at the NK and the MR sites show  $R^2$  between 0.8686 and 0.9972, supporting the hypothesis of similar sources at the sampling sites and of non-combustion traffic emissions as main source. The  $EF_{Sb}$  and those of typical tracers of brakes (i.e., Fe, Cu and Ba) show similar and very high  $R^2$  ( $R^2$  between 0.9949 and 0.9972), suggesting that non-exhaust traffic emissions are the dominant source for these elements in urban  $PM_{10}$  in London.

Re-suspension of small particles of road dust may have a significant effect on the generation of  $PM_{10}$  enriched in metals (Amato et al., 2014; Thorpe and Harrison, 2008). The road dust samples collected at the MR site (MRRD-1, MRRD-2 and MRRD-3) are enriched in Fe, Cu, Zn, Sb, Ba, Cr and Pb compared to road dust at the NK site (NKRD-1, NKRD-2 and NKRD-3) (Table 3), most probably reflecting the higher traffic density. This observation supports the idea that re-suspended road dust is an important source of these elements in urban PM (Amato et al., 2014).

Brake wear is the dominant source of Ba in urban and natural PM (Gietl and Klemm, 2009; Gietl et al., 2010; Iijima et al., 2007; Moreno et al., 2015). We find high concentrations of Ba in brakes ( $310 - 1300 \mu g g^{-1}$ ) and samples of manhole cover ( $120-1100 \mu g g^{-1}$ ) (Table 2). The concentrations of Ba in the  $PM_{10}$  at the NK site ( $1.6 \pm 0.4 ng m^{-3}$ ) are much lower than at the MR site ( $5.7 - 84 ng m^{-3}$ ), supporting the dominant contribution of brake wear.

The concentration of Zn in  $PM_{10}$  ranges between  $1.4$  and  $3.1 ng m^{-3}$  at the NK site, and between  $3.7$  and  $41 ng m^{-3}$  at the MR site. The concentration of Cu in  $PM_{10}$  ranges between  $1.9$  and  $3.6 ng m^{-3}$  at the NK site and between  $9.4$  and  $130 ng m^{-3}$  at the MR site. The element concentrations show that the content of Zn in tires and of Cu in brakes, tires and manhole cover are significantly higher than in other sources (Table 2). In addition, samples of road tarmac surface and manhole cover contain significant amounts of Zn. Cu/Sb ratios between 3.3 and 9.1 have been used to identify brake wear in PM collected in Cologne, London, Stockholm and Budapest (Hjortenkrans et al., 2007; Salma and Maenhaut, 2006; Weckwerth, 2001). In this study similar Cu/Sb ratios are observed in  $PM_{10}$ , although with a smaller range between 5.8 and 8.3 (Table 1). The average Cu/Sb ratios in the  $PM_{10}$  at the NK site are slightly higher than those in the  $PM_{10}$  at the MR site. However, the Cu/Sb ratios in the studied brake pads range between 27 and 39 and are large compared with typical values for brakes in PM (Table 2). This observation is likely explained by the recent restrictions on the use of  $Sb_2S_3$  during the manufacturing process of brake pads due to its potential carcinogenic properties (Hüner et al., 2001).

The concentrations of Cr in  $PM_{10}$  collected at the MR site ( $0.9 - 8.2 ng m^{-3}$ ) are higher than those at the NK site ( $0.3 \pm 0.1 ng m^{-3}$ ). Multiple sources including brakes, manhole cover, yellow road paint (NKRP-2) and road dust are enriched in this element relative to natural dust (Table 3). However, the positive correlation between the  $EF_{Sb}$  and the  $EF_{Cr}$  ( $R^2 = 0.9385$ ) in  $PM_{10}$  (Figure 1), and between the  $EF_{Sb}$  and those of other elements linked with non-exhaust traffic emissions, i.e., Cu, Ba, and Fe, suggests that not only Cu, Ba and Fe, but also Cr is mainly controlled by non-exhaust traffic emissions in the urban atmosphere. The concentrations of Fe and  $EF_{Fe}$  in the  $PM_{10}$  collected at MR are higher than those in the  $PM_{10}$  at NK, and significantly larger concentrations of this element are found in samples of brakes and manhole cover. In addition to these sources, brake discs contribute significantly to  $PM_{10}$  enriched in Fe (Wählin et al., 2006).

The elemental concentrations and EF of Ni and V are similar in the  $PM_{10}$  at both sites, which suggests that

these elements are not directly affected by the density of traffic (Tables 1 and 3). Previous studies suggested that Ni and V are mainly derived from fuel oil, gas refineries, and industrial processes (Moreno et al., 2010; Nriagu and Pacyna, 1988; Peltier and Lippmann, 2010), and less from non-exhaust traffic sources (Thorpe and Harrison, 2008). In a recent receptor modeling study conducted using PM<sub>10</sub> samples collected at the NK site (Beddows et al., 2015), Ni and V were found to be associated with high concentrations of sulphate in a fuel oil-related factor.

Lead concentrations in PM<sub>10</sub> are slightly higher at the MR site (1.1-8.8 ng m<sup>-3</sup>) compared to the NK site (1.0±0.3 ng m<sup>-3</sup>) but the EF<sub>Pb</sub> are similar at both sites. Some studies based on emissions of metals in PM<sub>10</sub> and PM<sub>2.5</sub> suggested that following the phasing out of leaded gasoline, Pb is emitted into the urban atmosphere from fuel and motor oil combustion or brake wear (Lough et al., 2005). Significantly high concentrations of Pb relative to other possible sources have been found in tires and brakes (4.0 – 38 µg g<sup>-1</sup>) and in manhole covers (56 – 690 µg g<sup>-1</sup>) (Table 2).

### 3.2 Source identification of lead using stable isotope ratios

The <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb isotope ratios determined in the PM<sub>10</sub> and the sources are shown in Table 4. Figure 2a shows that the Pb isotope ratios in PM<sub>10</sub> are similar at the MR and NK sites. This observation, and similarity between the EF<sub>Pb</sub> in the PM<sub>10</sub> at the MR and NK sites (Table 1), suggest that the source(s) at NK and MR sites are the same. The Pb isotope ratios measured in the PM<sub>10</sub> at NK (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.446-17.598, <sup>206</sup>Pb/<sup>207</sup>Pb = 1.1218 – 1.1304, <sup>208</sup>Pb/<sup>206</sup>Pb = 2.1288 – 2.1382) fall within the respective ranges at MR (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.305 – 17.701, <sup>206</sup>Pb/<sup>207</sup>Pb = 1.1137 – 1.1364, <sup>208</sup>Pb/<sup>206</sup>Pb = 2.1246 – 2.1476). These Pb signatures are significantly different from those of natural sources in the UK (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.18 – 1.19, Monna et al., 1997), which suggests an ongoing contribution of anthropogenic sources of Pb in atmospheric PM. The <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>206</sup>Pb/<sup>207</sup>Pb isotope ratios determined in our study are similar to those reported in 1995, 1998 and 1999 and partly overlap with years 1996, 2000 and 2001 (Monna et al., 1997; Noble et al., 2008) (Figure 2b). The <sup>206</sup>Pb/<sup>207</sup>Pb determined for urban PM<sub>10</sub> in our study fall within the range determined in France and the UK during mid-90s, that ranged between 1.1008 and 1.1453 (Monna et al., 1997). Noble et al. (2008) showed that since leaded gasoline was banned in the UK in 1998, the <sup>206</sup>Pb/<sup>207</sup>Pb isotope ratio in urban PM in London shifted slightly from 1.1169 – 1.1388 to more radiogenic ratios during 2000 and 2001, and they stabilized thereafter (1.1354 – 1.1507). The isotope ratios of road paint (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.866 – 18.301, <sup>206</sup>Pb/<sup>207</sup>Pb = 1.1471 – 1.1708, <sup>208</sup>Pb/<sup>206</sup>Pb = 2.0843 – 2.1012) and of road dust (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.347 – 17.890, <sup>206</sup>Pb/<sup>207</sup>Pb = 1.1163 – 1.1417, <sup>208</sup>Pb/<sup>206</sup>Pb = 2.1176 – 2.1446) collected at the two sampling sites show significant Pb isotope ratio variability. As illustrated in Figure 2a, the Pb isotope ratios of the PM<sub>10</sub> fall on a mixing line with gasoline used in the UK before its phasing out as one end member (Monna et al., 1997), and road dust which contains re-mobilized Pb from leaded gasoline and other source deposits such as tires, brakes and road furniture as the other end member. The Pb isotope composition of the PM<sub>10</sub> collected at NK and MR sites is similar to those of road dust and manhole cover which suggests that re-suspended road dust may contribute to Pb enrichment in urban PM. Previous elemental analyses of PM<sub>10</sub> from the NK site showed appreciable concentrations of crustal elements such as Al and Ca, that might have arisen from road dust (Beddows et al., 2015). Therefore, it seems likely that road dust with residual contamination from the earlier use of leaded gasoline contribute to PM<sub>10</sub> due to resuspension into the atmosphere.

### 3.3 Copper and zinc isotope ratios variations in source materials and PM<sub>10</sub>

The Cu and Zn isotope ratios of PM<sub>10</sub> collected at the sites with high and low traffic densities and the potential local sources are illustrated in Figure 3. Previous published data for PM<sub>2.5-80</sub> collected in London between 2014 and 2015 and for PM<sub>10</sub> collected in Barcelona between 2012 and 2013 (Ochoa Gonzalez et al., 2016) are shown for reference. The  $\delta^{65}\text{Cu}_{\text{NIST976}}$  values vary in the range between  $+0.01\pm 0.13\text{‰}$  and  $+0.51\pm 0.10\text{‰}$  at the MR site and between  $-0.01\pm 0.10\text{‰}$  and  $+0.46\pm 0.07\text{‰}$  at the NK site which suggests same sources of Cu in the PM<sub>10</sub> collected at the two sampling sites (Table S2-Sn). This agrees with our hypothesis derived from the linear correlations between the EF of typical tracers of non-exhaust emissions (i.e. Cu, Sb, Ba, Zn and Fe) in PM<sub>10</sub> (Figure 1). The  $\delta^{66}\text{Zn}_{\text{Lyon}}$  values in PM<sub>10</sub> collected at the MR site range between  $-0.14\pm 0.04\text{‰}$  and  $+0.33\pm 0.04\text{‰}$ , and at the NK site between  $-0.21\pm 0.14\text{‰}$  and  $+0.26\pm 0.12\text{‰}$ . We do not observe a significant temporal trend in the isotope composition during the sampling period of 20 days and there is no correlation between the shifts in the isotopic composition of Cu and those of Zn (Table S2-Sn). The latter observation probably reflects different contribution from the non-exhaust traffic sources of Zn and those of Cu. Although higher Cu and Zn concentrations are found at the high traffic site (Table 1), the isotope data set suggests that the dominant sources and/or controlling processes are the same at both sites studied. The similar variability in the Cu and Zn isotope ratios in the PM<sub>10</sub> collected at the low and high traffic sites during 3 weeks over July 2010 (Figure 3) suggests that the sources of Cu and Zn in PM<sub>10</sub> do not change on that temporal and spatial scale. This observation is in good agreement with previous studies over an entire year that showed only significant Cu isotope variability during the winter season and suggested that traffic sources are the main contributor to Cu and Zn enrichment in PM<sub>2.5-80</sub> (Ochoa Gonzalez et al., 2016) and PM<sub>2.5-10</sub> (Visser et al., 2015) in London. The Cu and Zn isotope ratios of PM<sub>2.5-80</sub> collected at building height during July and August 2014 and July and August 2015 showed  $\delta^{65}\text{Cu}_{\text{NIST976}}$  between  $+0.46\pm 0.12\text{‰}$  and  $+0.55\pm 0.15\text{‰}$  and  $\delta^{66}\text{Zn}_{\text{Lyon}}$  between  $+0.02\pm 0.04\text{‰}$  and  $+0.17\pm 0.02\text{‰}$ , with one light sample collected during summer 2015 ( $\delta^{66}\text{Zn}_{\text{Lyon}} = -0.29\pm 0.04\text{‰}$ ) (Ochoa Gonzalez et al., 2016). The Cu and Zn isotope signatures in PM<sub>10</sub> collected in London at the NK and MR sites during 2010 in London agree well with the isotope signatures in PM<sub>2.5-80</sub> collected in another street canyon during 2014 and 2015 in the same city (Ochoa Gonzalez et al., 2016).

#### 3.3.1 Controls of copper isotope signatures in urban particulate matter in London

Brakes, tires, manhole cover, road paint, and road tarmac surface have  $\delta^{65}\text{Cu}_{\text{NIST976}}$  values ranging between  $-0.18\pm 0.14\text{‰}$  and  $+0.71\pm 0.09\text{‰}$  (Table S2-Sn). Four out of the six road dust samples show Cu isotope signatures falling within this range and two samples show more negative isotope signatures ( $\delta^{65}\text{Cu}_{\text{NBS976}} = -0.28\pm 0.08\text{‰}$  and  $-0.22\pm 0.08\text{‰}$ ) at the MR site. Isotopically heavy Cu is found in road paint, road tarmac surface and selected samples of brakes and manhole cover, with  $\delta^{65}\text{Cu}_{\text{NBS976}}$  values above  $+0.55\text{‰}$ . The  $\delta^{65}\text{Cu}_{\text{NIST976}}$  of the non-exhaust traffic sources (i.e., tires and brakes) show significant isotope variability, ranging between  $+0.17\pm 0.10\text{‰}$  and  $+0.33\pm 0.12\text{‰}$  for tires and between  $+0.28\pm 0.10\text{‰}$  and  $+0.63\pm 0.14\text{‰}$  for brakes, most probably reflecting the different Cu species such as metallic Cu, Cu oxides or Cu sulfides (Grigoratos and Martini, 2015; Straffelini et al., 2015), the different geographical location of the ores used and/or possible isotopic fractionation during the manufacturing processes.

Cu/Sb ratios in the PM have been used to identify source contribution of brake wear in urban PM

(Hjortenkran et al., 2007; Salma and Maenhaut, 2006; Weckwerth, 2001). The relationship between Cu/Sb ratios and the Cu isotope composition in the samples of PM analysed during this work and a previous study conducted in Barcelona and London (Ochoa Gonzalez et al., 2016) is illustrated in Figure 4. The PM<sub>10</sub> samples from Barcelona and London with low Cu/Sb ratios ranging between 5.8 and 12, which fall within the range of Cu/Sb found for brakes, have isotopically lighter Cu with  $\delta^{65}\text{Cu}_{\text{NBS976}}$  ranging between -0.01 and +0.51 ‰. Indeed, these isotope signatures largely overlap with the Cu isotope signatures in samples of brakes analyzed during this study ( $\delta^{65}\text{Cu}_{\text{NIST976}} = +0.28 \pm 10\text{‰} - +0.63 \pm 14\text{‰}$ ) (Table S2-Sn). Coarse particles (PM<sub>2.5-80</sub>) in London with Cu/Sb ratios larger than 12 and isotopically heavier Cu ( $\delta^{65}\text{Cu}_{\text{NIST976}}$  ranging between +0.63 and +0.97 ‰) were attributed to particles emitted during fossil fuel combustion emissions which seemed more important during end-autumn and the winter season (Ochoa Gonzalez et al., 2016).

### 3.3.2 Controls of zinc isotope signatures in urban particulate matter in London

Brakes, tires, manhole cover, road paint, and road tarmac surface show  $\delta^{66}\text{Zn}_{\text{Lyon}}$  ranging between -0.02±0.09 ‰ and +0.58±0.10 ‰ (Table S2-Sn). The Zn isotope signatures of the samples of road dust range between +0.21±0.05 ‰ and +0.34±0.10 ‰ at both sites, except one sample with a  $\delta^{66}\text{Zn}_{\text{Lyon}}$  of -0.03±0.08 ‰ at the NK site. These ratios overlap with the signatures in PM<sub>10</sub> at the NK and MR sites. The variations in the Zn isotope signatures found in the road dust samples at the two sites likely reflect the potential accumulation of different sources. Manhole cover, road paint and road surface show significant isotope variability within each source type, up to 0.51 ‰. This suggests that the source materials and/or processes during the manufacturing of these products have an effect on the isotope variability of each kind of source. The isotopically heaviest Zn has been measured in road paint ( $\delta^{66}\text{Zn}_{\text{Lyon}}$  between +0.07 and +0.58 ‰, n=4). The Zn isotope composition of brakes and tires vary within a small range with  $\delta^{66}\text{Zn}_{\text{Lyon}}$  between +0.15±0.07 ‰ and +0.21±0.08 ‰ (n=6) and are not significantly different relative to an average internal precision of 0.08 ‰. Together with the high levels of Zn in tires (Table 2), we propose that Zn in most of the PM<sub>10</sub> sampled at the NK and the MR sites ( $\delta^{66}\text{Zn}_{\text{Lyon}}$  ranging between -0.04±0.14 ‰ and +0.33±0.04 ‰) are derived from tires (Figure 3). However, a source enriched in isotopically light Zn which can explain the Zn isotope signatures found in three samples of PM<sub>10</sub>, i.e., in NK3, NK7 and MR8 (Figure 3) has not been identified. The isotopic composition of Zn in PM<sub>10</sub> in London is similar to that of PM<sub>2.5-80</sub> collected at a high density traffic site in the same city during 2014 and 2015, with  $\delta^{66}\text{Zn}_{\text{Lyon}}$  ranging between -0.29 ‰ and +0.17 ‰ (Figure 3). The  $\delta^{66}\text{Zn}_{\text{Lyon}}$  in bus air filters analysed during previous studies (Cloquet et al., 2006) overlap with the signatures in the PM<sub>10</sub> collected at the NK and MR sites, whereas those of gasoline (Gioia et al., 2008) only overlap with three samples of PM<sub>10</sub> out of 18 (NK3, NK7 and MR8) (Figure 3, Table S2-Sn). The relatively constant traffic densities and the similar Zn/Sb ratios in PM<sub>10</sub> at each sampling site (Table 2) suggest that contribution from gasoline combustion is less likely, in line with the typically low concentrations of Zn found in gasoline (Pignatola et al., 2005). The light Zn isotope signatures found in PM<sub>10</sub> in Barcelona ( $\delta^{66}\text{Zn}_{\text{Lyon}} = -0.83 - -0.45\text{‰}$ ) were tentatively attributed to metallurgical emissions (Ochoa Gonzalez et al., 2016). This hypothesis agrees with previous observations pointing that industrial processes such as smelting or combustion exert an effect on the fractionation due to evaporation and/or condensation processes (Mattielli 2009; Bigalke 2010; Ochoa Gonzalez and Weiss, 2015; Thapalia et al., 2015). These findings suggest that tire wear largely contribute to Zn in PM<sub>10</sub> in London, whereas for some samples the isotope signatures suggest a minor contribution from high temperature industrial

or fossil fuel combustion.

#### 4. Conclusions

The aim of this study was to determine the short-term temporal and spatial isotope variability of Cu, Zn and Pb in urban PM<sub>10</sub> collected at two sites with different traffic densities in central London, UK, and in possible sources, including non-combustion traffic emissions (tires and brakes), road furniture (road paint, manhole cover and road tarmac surface) and road dust. Samples of PM<sub>10</sub> and possible sources were also characterized for the EF of other metals (Ni, V, Fe, Sb, Ba and Cr) to assist the source apportionment study. Copper and Zn concentrations and EF in the PM<sub>10</sub> were higher at the sampling location with high traffic density, along with other elements commonly associated with traffic related sources including Fe, Sb, Ba and Cr. In contrast, the EF of Pb showed no significant differences between the two sites although was enriched relative to crustal values.

The <sup>206</sup>Pb/<sup>207</sup>Pb in the PM<sub>10</sub> ranges between 1.1137 and 1.1364, and the isotope ratios of Cu and Zn expressed as  $\delta^{65}\text{Cu}_{\text{NIST976}}$  and  $\delta^{66}\text{Zn}_{\text{Lyon}}$  range between -0.01 and +0.51 ‰ and between -0.21 and +0.33 ‰, respectively. The results indicate that traffic density does not exert a significant effect on the observed isotope signatures, suggesting similar sources for these toxic metals at both sites. The Pb isotope signatures of the PM<sub>10</sub> collected at the NK and MR sites overlap with those of road dust which suggests that re-suspended road dust is an important source. The similarity between the Cu isotope signatures in samples of PM<sub>10</sub> ( $\delta^{65}\text{Cu}_{\text{NBS976}}$  ranging between -0.01±0.10 ‰ and +0.51±0.10 ‰) and brakes ( $\delta^{65}\text{Cu}_{\text{NIST976}}$  ranging between +0.28±0.10 ‰ and +0.63±0.14 ‰), and the low Cu/Sb ratios (Cu/Sb ranging between 5.8 and 12) which fall within the range of Cu/Sb found for brakes, suggest that brake wear is the dominant source of Cu. The Zn isotope signatures in PM<sub>10</sub> at NK and MR overlap with the signatures of tires and road dust but additional sources such as high temperature industrial emissions that impart isotopically light Zn, need to be invoked to explain the light signatures found in 3 out of 18 samples.

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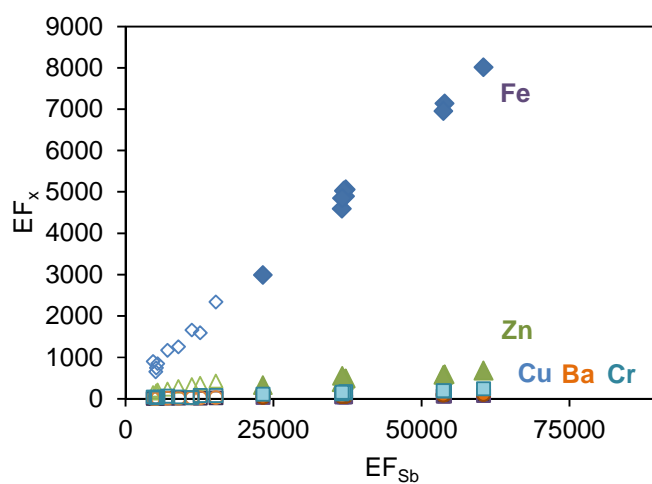
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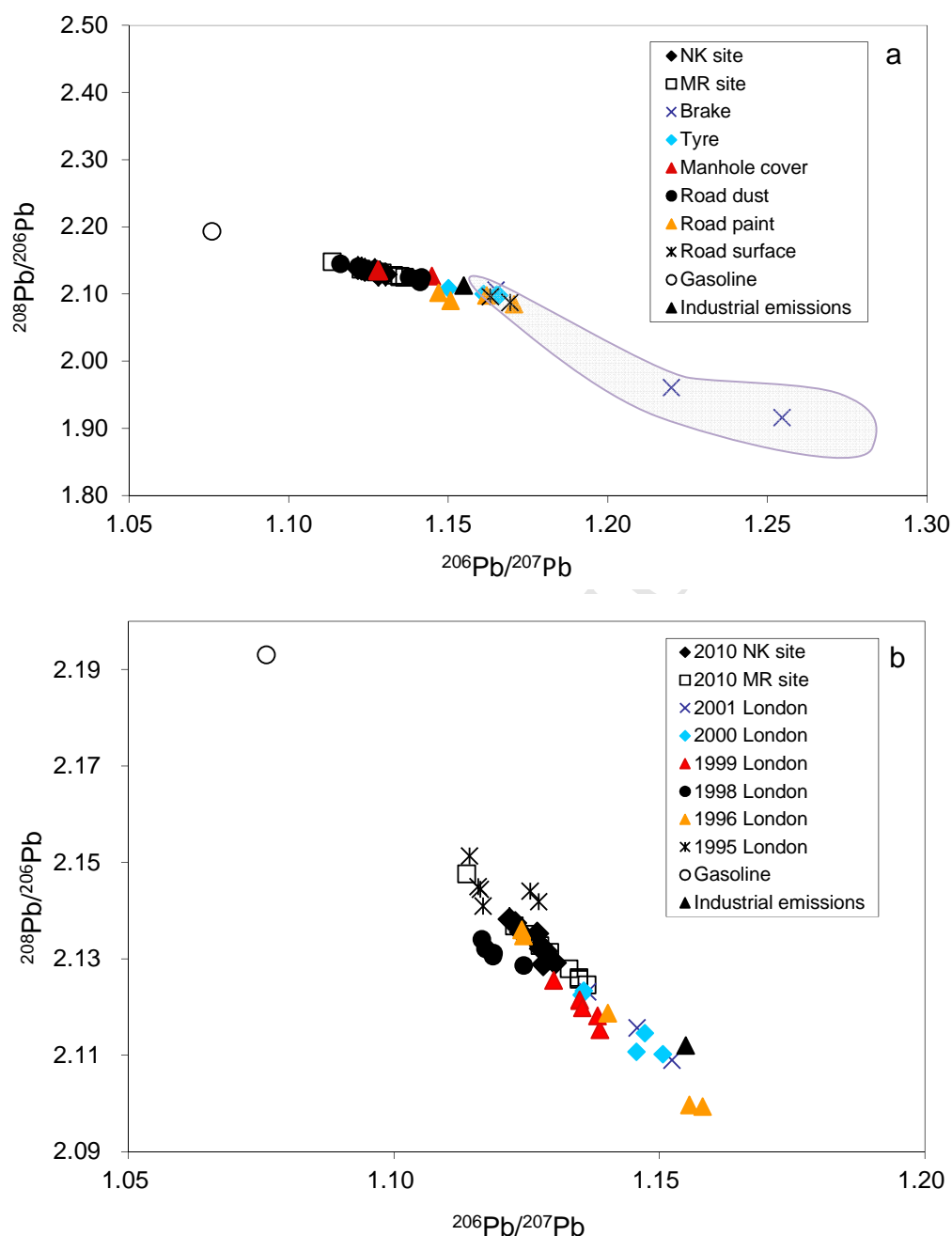


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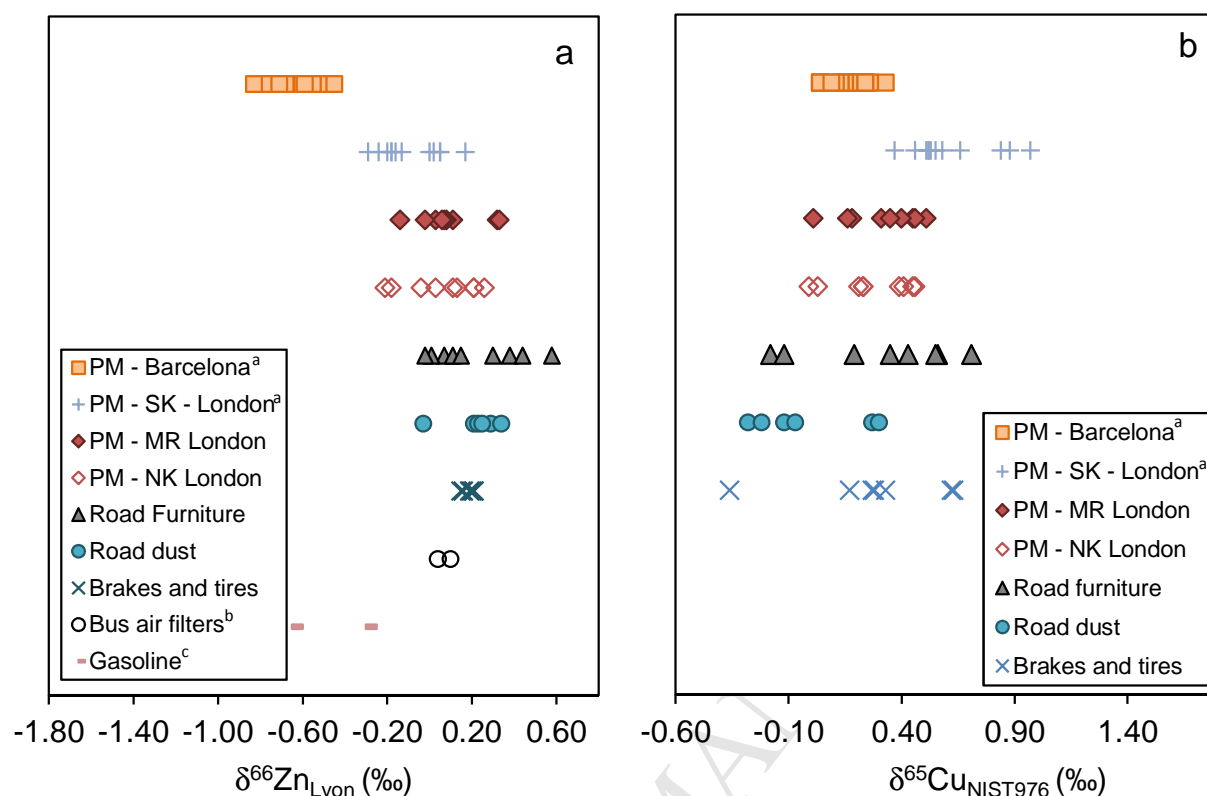
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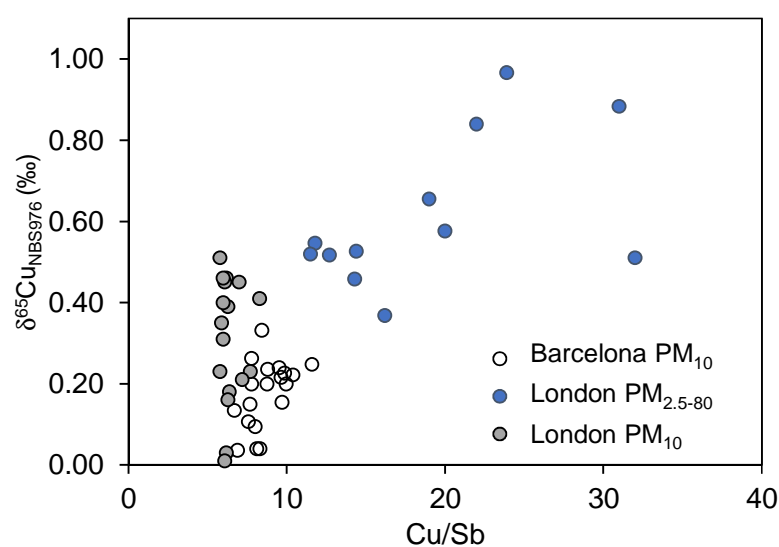
**Figure 1.** Relationship between the enrichment factors of Sb ( $EF_{Sb}$ ) and  $EF_{Fe}$  ( $R^2=0.9960$ ),  $EF_{Cu}$  ( $R^2=0.9972$ ),  $EF_{Zn}$  ( $R^2=0.8686$ ),  $EF_{Ba}$  ( $R^2=0.9949$ ) and  $EF_{Cr}$  ( $R^2=0.9385$ ) in the  $PM_{10}$  collected in North Kensington (open symbols) and Marylebone Road (closed symbols).



**Figure 2.** (a)  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  plot of the PM<sub>10</sub> samples collected in Marylebone (MR site) and North Kensington (NK site) and possible sources in this study; (b)  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  plot of the PM<sub>10</sub> measured in London since the phasing out of leaded gasoline between 1996 and 2001, as well as gasoline and industrial emissions (Noble et al., 2008 and Monna et al., 1997) and during 2010 (this study). 2SD are not displayed in the figure as they are small and fall within the marker dimensions.



**Figure 3.** Zinc (a) and Cu (b) isotopic composition in PM<sub>10</sub> collected at the NK site (PM-NK London) and the MR site (PM-MR London) and local sources during this study (summer 2010). Average 2SD for Zn and Cu isotope measurements are 0.08 and 0.10‰, respectively. Also shown are previous published Zn and Cu isotope signatures in atmospheric PM<sub>2.5-80</sub> collected in South Kensington in London during 18 months between 2014 and 2015 (PM – SK – London), and PM<sub>10</sub> collected in Barcelona during two sampling campaigns in 2012 and 2013 labelled as PM - Barcelona (Ochoa Gonzalez et al., 2016)<sup>a</sup> with average 2SD for Zn and Cu isotope ratios of 0.08 and 0.11‰, respectively. The Zn isotope composition of gasoline (Gioia et al., 2008)<sup>b</sup> and that from exhaust emissions represented by previously analyzed bus air filters (Cloquet et al., 2006)<sup>c</sup> are also shown. The Cu isotope signatures in PM collected during the winter season in London (PM – SK – London) are highlighted as they shown heavier values, explained by an increasing fossil fuel combustion. Previously published Zn isotope ratios referring to the IRMM-3702 standard were recalculated to JMC 3-0749L Lyon using an isotopic offset of +0.32‰ for Zn (Moeller et al., 2012).



**Figure 4.** Relationship between Cu/Sb ratios and  $\delta^{65}\text{Cu}_{\text{NIST976}}$  in PM<sub>10</sub> collected at the NK site and the MR site in this study (London PM<sub>10</sub>), and previous publish data in PM<sub>2.5-80</sub> from London (London PM<sub>2.5-80</sub>) and in PM<sub>10</sub> from Barcelona (Ochoa Gonzalez et al., 2016).

**Table 1.** Concentrations of PM<sub>10</sub>, major and trace elements in the PM<sub>10</sub> samples collected in Marylebone (MR) and North Kensington (NK), and Cu/Sb ratios.

Sample	Reference	Concentrations											Cu/Sb
		PM <sub>10</sub> ( $\mu\text{g m}^{-3}$ )	Fe ( $\text{ng m}^{-3}$ )	Al ( $\text{ng m}^{-3}$ )	Cu ( $\text{ng m}^{-3}$ )	Zn ( $\text{ng m}^{-3}$ )	Sb ( $\text{ng m}^{-3}$ )	Ba ( $\text{ng m}^{-3}$ )	Pb ( $\text{ng m}^{-3}$ )	Cr ( $\text{ng m}^{-3}$ )	Ni ( $\text{ng m}^{-3}$ )	V ( $\text{ng m}^{-3}$ )	
NK - PM <sub>10</sub>	NK1	12	79	23	3.1	2.9	0.5	2.0	1.3	0.2	0.5	0.7	6.2
	NK2	12	46	14	2.3	1.4	0.3	1.1	0.6	0.3	0.4	0.5	7.7
	NK3	10	66	13	3.1	2.7	0.5	1.7	1.3	0.2	0.2	0.3	6.2
	NK4	17	58	12	2.5	1.8	0.3	1.6	0.8	0.4	0.3	0.4	8.3
	NK5	15	46	6.1	1.9	1.4	0.3	1.2	0.7	0.1	0.2	0.2	6.3
	NK6	17	89	22	3.5	3.1	0.5	2.0	1.1	0.3	0.4	0.6	7.0
	NK7	15	68	8.2	3.6	2.3	0.5	1.9	0.9	0.3	0.2	0.2	7.2
	NK8	12	58	8.6	2.5	2.2	0.4	1.5	1.2	0.3	0.2	0.1	6.3
	NK9	14	87	29	3.5	2.8	0.6	1.8	1.4	0.4	0.2	0.1	5.8
Average $\pm$ SD		14 $\pm$ 3	66 $\pm$ 16	15 $\pm$ 8	2.9 $\pm$ 0.6	2.3 $\pm$ 0.6	0.4 $\pm$ 0.1	1.6 $\pm$ 0.4	1.0 $\pm$ 0.3	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	0.3 $\pm$ 0.2	6.8 $\pm$ 0.9
MR - PM <sub>10</sub>	MR1	37	2660	150	130	41	22	84	8.8	8.2	3.6	2.6	5.8
	MR2	28	550	20	26	8.0	4.3	18	1.1	1.7	0.7	0.6	6.1
	MR3	29	436	24	21	7.8	3.5	14	1.9	1.5	0.6	0.4	6.1
	MR4	38	481	25	24	8.4	3.7	15	1.4	1.9	0.9	0.4	6.4
	MR5	29	494	16	24	7.3	3.9	16	1.3	1.7	0.7	0.3	6.0
	MR6	41	641	35	33	11	5.2	20	1.8	2.5	1.0	0.8	6.3
	MR7	34	2300	89	110	35	19	72	6.8	7.8	2.7	1.5	6.0
	MR8	27	279	15	13	5.5	2.2	7.9	1.7	1.1	0.3	0.2	6.0
	MR9	18	212	17	9.4	3.7	1.6	5.7	1.2	0.9	0.3	0.1	5.9
Average $\pm$ SD		31 $\pm$ 7	-	-	-	-	-	-	-	-	-	-	6.1 $\pm$ 0.2



**Table 2.** Concentrations of major and trace elements in local sources close to Marylebone (MR) and North Kensington (NK), including Cu/Sb ratios. ‘<’ means below detection limit; ‘-’ means not calculated.

Sample	Reference	Concentrations										Cu/Sb
		Fe (mg g <sup>-1</sup> )	Al (mg g <sup>-1</sup> )	Cu (μg g <sup>-1</sup> )	Zn (μg g <sup>-1</sup> )	Sb (μg g <sup>-1</sup> )	Ba (μg g <sup>-1</sup> )	Pb (μg g <sup>-1</sup> )	Cr (μg g <sup>-1</sup> )	Ni (μg g <sup>-1</sup> )	V (μg g <sup>-1</sup> )	
Brake	FSB-1	6.8	9.5	6.1	20	0.2	1000	5.3	89	51	9.7	27
	FSB-2	5.2	7.1	4.4	17	0.1	1300	4.0	80	41	7.0	39
	HBP-1	89	5.5	25	46	0.8	310	38	110	28	15	30
Tire	R43/54-1	0.4	0.2	43	8100	<	12	9.9	<	<	<	-
	R43/54-2	0.3	0.3	41	13000	<	19	14	<	1.4	<	-
	R56/57-1	0.2	0.4	26	7400	<	2.1	9.1	<	<	<	-
Manhole cover	NKMHC-1	68	5.7	52	370	7.4	550	690	130	100	26	7.0
	NKMHC-2	25	2.8	20	130	3.6	1100	56	93	86	15	5.4
	MRMHC-1	52	5.2	170	530	17	120	210	2300	1700	76	9.9
	MRMHC-2	43	1.5	89	420	7.5	120	89	120	110	120	12
Road dust	NKRD-1	9.4	4.4	70	220	3.3	93	140	29	11	19	21
	NKRD-2	7.6	3.2	17	80	1.0	34	22	29	100	15	17
	NKRD-3	18	13	25	170	0.7	86	26	31	18	56	35
	MRRD-1	17	6.0	800	560	21	160	410	55	26	23	38
	MRRD-2	14	3.7	74	350	10	97	170	54	13	15	7.3
	MRRD-3	10	4.0	140	350	40	94	54	40	17	14	3.5
Road paint	NKRP-1	0.6	0.3	1.8	44	<	2.4	2.8	3.2	4.0	0.5	-
	NKRP-2	0.4	0.2	<	4.8	93	200	3100	840	3.4	0.7	-
	MRRP-1	0.7	0.3	4.3	14	0.5	6.1	3.8	1.1	2.4	0.7	8.6
	MRRP-2	1.3	2.4	2.6	14	<	5.4	2.9	1.3	6.6	1.9	-
Road tarmac surface	NKRS-1	8.2	4.9	7.1	40	0.4	64	11	16	15	28	18
	NKRS-2	7.3	4.4	5.2	34	0.3	100	8.8	20	19	21	17

**Table 3.** Enrichment factors (EFs) in local sources and the PM<sub>10</sub> samples collected at Marylebone (MR) and North Kensington (NK) sites. ‘-’ means not calculated.

Sample	Reference	EFs								
		Fe	Cu	Zn	Sb	Ba	Pb	Cr	Ni	V
NK - PM <sub>10</sub>	NK1	8.7	740	190	5300	10	258	18	83	44
	NK2	8.2	900	150	4700	9.0	199	47	110	54
	NK3	12	1300	300	9000	15	458	41	68	31
	NK4	13	1200	230	7100	16	317	67	100	45
	NK5	19	1700	340	11000	22	485	26	110	55
	NK6	10	850	210	5500	11	220	33	72	36
	NK7	21	2300	430	15000	27	484	81	95	37
	NK8	17	1600	380	13000	20	663	80	100	25
	NK9	7.6	650	150	5200	7.3	225	34	28	7.0
	Average±SD	13±5	1200±600	300±200	8000±4000	15±7	400±200	50±30	90±30	40±20
MR - PM <sub>10</sub>	MR1	45	4600	410	37000	65	270	120	100	25
	MR2	69	7100	600	54000	100	245	190	150	44
	MR3	46	4900	490	37000	66	362	140	110	22
	MR4	48	5100	490	37000	69	247	170	150	25
	MR5	78	8000	680	61000	110	366	240	180	31
	MR6	46	5000	450	37000	66	232	160	120	31
	MR7	65	7000	580	54000	93	348	190	130	25
	MR8	47	4800	560	37000	62	518	160	93	19
	MR9	31	3000	330	23000	39	334	120	64	13
	Average±SD	50±20	6000±2000	500±200	40000±20000	70±30	330±90	170±40	130±40	26±9
Brake	FSB-1	1.8	3.5	3.2	5.9	13	2.6	21	22	1.5
	FSB-2	1.9	3.3	3.5	3.9	21	2.6	25	24	1.4
	HBP-1	41	25	13	37	6.6	32	46	21	3.9
Tire	R43/54-1	4.6	1200	60000	-	6.9	230	-	-	-
	R43/54-2	2.6	780	69000	-	7.5	220	-	21	-
	R56/57-1	1.5	400	31000	-	0.7	110	-	-	-
Manhole cover	NKMHC-1	30	49	97	330	11	550	50	75	6.6
	NKMHC-2	23	38	72	320	44	92	74	130	8.1
	MRMHC-1	25	170	150	800	2.7	180	970	1400	21
	MRMHC-2	73	330	420	1300	9.1	280	190	310	120
Road dust	NKRD-1	5.3	85	73	190	2.4	140	14	10	6.3
	NKRD-2	6.0	29	37	79	1.2	32	20	131	6.8
	NKRD-3	3.6	10	19	14	0.8	9.0	5.2	5.8	6.4
	MRRD-1	7	730	140	880	3.2	300	21	18	5.7
	MRRD-2	9.5	110	140	680	3.0	200	32	14	5.9
	MRRD-3	6.3	190	130	2500	2.7	62	22	17	5.3
Road paint	NKRP-1	4.6	28	190	-	0.8	37	21	48	2.2
	NKRP-2	5.1	-	39	130000	120	76000	10000	76	5.4
	MRRP-1	7.0	88	80	450	2.7	67	9.6	39	3.9
	MRRP-2	1.4	5.8	8.5	-	0.3	5.5	1.2	11	1.1
Road surface	NKRS-1	4.2	7.9	12	22	1.5	11	7.3	13	8.3
	NKRS-2	4.2	6.4	12	18	2.8	9.2	10	18	7.1

**Table 4.** Lead isotope ratios of PM<sub>10</sub> samples collected at Marylebone Road (MR) and North Kensington (NK) and sources analyzed during this study. Each sample has been measured 3 or 4 times to calculate the 2SD.

Sample	Sample ID	Pb isotope ratios					
		<sup>206</sup> Pb/ <sup>204</sup> Pb	2SD	<sup>206</sup> Pb/ <sup>207</sup> Pb	2SD	<sup>208</sup> Pb/ <sup>206</sup> Pb	2SD
NK - PM <sub>10</sub>	NK1	17.446	0.004	1.1218	0.0001	2.1382	0.0002
	NK2	17.552	0.003	1.1277	0.0001	2.1327	0.0002
	NK3	17.465	0.005	1.1229	0.0001	2.1374	0.0002
	NK4	17.537	0.002	1.1270	0.0001	2.1352	0.0001
	NK5	17.554	0.003	1.1277	0.0001	2.1321	0.0001
	NK6	17.569	0.004	1.1287	0.0001	2.1315	0.0001
	NK7	17.598	0.004	1.1304	0.0001	2.1291	0.0001
	NK8	17.487	0.004	1.1239	0.0001	2.1355	0.0001
	NK9	17.564	0.003	1.1282	0.0001	2.1288	0.0001
MR - PM <sub>10</sub>	MR1	17.512	0.002	1.1256	0.0001	2.1351	0.0001
	MR2	17.643	0.005	1.1330	0.0001	2.1279	0.0001
	MR3	17.581	0.005	1.1294	0.0001	2.1313	0.0002
	MR4	17.677	0.003	1.1349	0.0001	2.1261	0.0001
	MR5	17.550	0.002	1.1275	0.0001	2.1327	0.0001
	MR6	17.678	0.002	1.1349	0.0001	2.1257	0.0002
	MR7	17.701	0.003	1.1364	0.0001	2.1246	0.0001
	MR8	17.463	0.001	1.1227	0.0001	2.1368	0.0002
	MR9	17.305	0.002	1.1137	0.0001	2.1476	0.0001
Brake	FSB-1	19.569	0.003	1.2200	0.0001	1.9598	0.0001
	FSB-2	20.199	0.002	1.2547	0.0001	1.9151	0.0001
	HBP-1	18.176	0.004	1.1651	0.0001	2.1052	0.0001
Tire	R30-1	17.937	0.003	1.1502	0.0001	2.1075	0.0002
	R43/54-1	18.190	0.002	1.1660	0.0001	2.0973	0.0001
	R43/54-2	18.181	0.002	1.1653	0.0001	2.0983	0.0001
	R56/57-1	18.138	0.002	1.1613	0.0001	2.0995	0.0002
Manhole cover	NKMHC-1	17.883	0.003	1.1450	0.0001	2.1262	0.0001
	NKMHC-2	17.547	0.004	1.1281	0.0001	2.1355	0.0002
	MRMHC-1	17.557	0.004	1.1284	0.0001	2.1332	0.0001
	MRMHC-2	17.550	0.002	1.1280	0.0001	2.1335	0.0002
Road dust	NKRD-1	17.438	0.002	1.1218	0.0001	2.1403	0.0001
	NKRD-2	17.762	0.001	1.1405	0.0001	2.1222	0.0002
	NKRD-3	17.728	0.002	1.1379	0.0001	2.1245	0.0001
	MRRD-1	17.890	0.003	1.1417	0.0001	2.1242	0.0001
	MRRD-2	17.777	0.002	1.1412	0.0001	2.1176	0.0002
	MRRD-3	17.347	0.002	1.1163	0.0001	2.1446	0.0001
Road paint	NKRP-1	17.930	0.002	1.1509	0.0001	2.0894	0.0001
	NKRP-2	18.301	0.002	1.1708	0.0001	2.0843	0.0001
	MRRP-1	17.866	0.001	1.1471	0.0001	2.1012	0.0001
	MRRP-2	18.135	0.001	1.1621	0.0001	2.0973	0.0002
Road tarmac surface	NKRS-1	18.148	0.001	1.1633	0.0001	2.0953	0.0001
	NKRS-2	18.252	0.001	1.1695	0.0001	2.0869	0.0001

Isotopic signatures in atmospheric particulate matter suggest important contributions from recycled gasoline for lead and non-exhaust traffic sources for copper and zinc in aerosols in London, United Kingdom

**Highlights**

- Isotope ratios of Cu, Zn and Pb were determined in PM<sub>10</sub> collected at two road sites with contrasting traffic densities in central London, UK, and in potential sources.
- Despite the different traffic densities, no significant differences in the isotope signatures of Cu, Zn and Pb are found in PM<sub>10</sub>, suggesting similar sources for each metal at both sites.
- Analysis of the isotopic composition of Cu, Zn and Pb in PM<sub>10</sub> and potential sources indicate important contributions from road dust resuspension, recycled leaded gasoline, tire and brake wear.